

Systematic Study of Hydration Patterns of Phosphoric (V) Acid and Its Mono-, Di- and Tripotassium Salts in Aqueous Solution

Maciej Śmiechowski, Emilia Gojło, Janusz Stangret

*Department of Physical Chemistry, Chemical Faculty, Gdańsk University of Technology,
Narutowicza 11/12, 80-952 Gdańsk, Poland
e-mail: msmiech@chem.pg.gda.pl*

The phosphate anions are of crucial importance in biological systems. Their universal role in the proper functioning of living organisms cannot be underestimated. Phosphates also find numerous applications in agricultural industry (as fertilizers), food industry (as soft drink additives) and cosmetic industry (as components in detergents and cleaning agents). Particularly, the dihydrogenphosphate anion plays a key role in the metabolic pathways, but all other phosphate forms present at varying acidity of the medium should be taken into account and thoroughly studied. Potassium is the most suitable cation of choice in this study, since its tendency to form ion pairs with phosphate anions appears to be negligible [1].

Ionic equilibria between the phosphate anions are complicated and involve multiple species and complexes [2]. The dihydrogenphosphate and hydrogenphosphate salts yield more than 99% of the principal anionic form, when dissolved in water. However, in the case of the phosphate anion, as well as phosphoric acid, the contribution of different phosphate forms is non-negligible, as predicted by simple balance based on H_3PO_4 dissociation constants [3].

Fourier transform infrared (FTIR) spectroscopy is a useful technique allowing the study of solute hydration. It has been successfully applied to study a wide range of electrolytes. By using isotopic dilution technique, HDO spectra can be obtained that are free from interpretative and experimental difficulties connected with H_2O spectra. The application of the difference spectra method proposed in our laboratory for results' analysis allows separation of the spectra of solute-affected HDO [4]. Here we apply FTIR spectroscopy of the OD band of HDO molecules to perform a systematic study of various phosphate forms in the order of decreasing protonation: $\text{H}_3\text{PO}_4 \rightarrow \text{KH}_2\text{PO}_4 \rightarrow \text{K}_2\text{HPO}_4 \rightarrow \text{K}_3\text{PO}_4$.

The position at maximum of the principal anion-affected HDO band for potassium phosphates moves in the order KH_2PO_4 (2614 cm^{-1}) > K_2HPO_4 (2447 cm^{-1}) > K_3PO_4 (2300 cm^{-1}) and remains in accordance with the previously determined linear dependence of OD band position on the polarizing power of the anion [5]. The number of moles of water affected by one mole of solute (N) equals 11.0, 11.9 and 16.2, respectively. The high coordination number of PO_4^{3-} in water has been recently inferred from neutron scattering studies [6]. Other important finding is that the isotopic substitution occurs also on the phosphate anions and phosphoric acid. The thus formed P-O-D groups interact with water molecules via strong hydrogen bonds and the relative strength of this interaction decreases with increasing anion charge. This and other plausible assignments of OD bands of HDO have been confirmed by calculating equilibrium structures of small aqueous clusters of the studied individuals utilising Density Functional Theory (DFT) with hybrid B3LYP functional and triple-zeta quality 6-311++G(d,p) basis set.

- [1] C.M. Preston, W.A. Adams, *J. Phys. Chem.* 83 (1979) 814-821.
- [2] J. Baril, J.-J. Max, C. Chapados, *Can. J. Chem.* 78 (2000) 490-507.
- [3] D.R. Lide (Ed.), *CRC Handbook of Chemistry and Physics*, 80th ed., CRC Press, Boca Raton, 1999, pp. 8-44-8-48.
- [4] J. Stangret, T. Gampe, *J. Phys. Chem. B* 103 (1999) 3778-3783.
- [5] J. Stangret, T. Gampe, *J. Phys. Chem. A* 106 (2002) 5393-5402.
- [6] P.E. Mason, J.M. Cruickshank, G.W. Neilson, P. Buchanan, *Phys. Chem. Chem. Phys.* 5 (2003) 4686-4690.